Ultra-high Extensibility of Deswollen Polysiloxane Networks with Supercoiled Structure (STATES AND STRUCTURES - Polymer Condensed States)

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The remarkable high extensibility of deswollen polysiloxane (PDMS) network crosslinked in solution with low concentration has been both theoretically and experimentally demonstrated. The uniaxial elongation of the deswollen network was carried out, and the elongation at break reached at ca. 1700%. This high extensibility originates from the two main factors: no or a negligible amount of trapped entanglements in the system due to the low preparation concentration; the reduction of end-to-end distance of network chains on deswelling. The fractal dimension (D) of the contracted network chains on deswelling (supercoiled chains) has been evaluated to be D=2.5 from the dependence of stress on elongation ratio on the basis of the concept of Pincus blob.

Keywords: Rubber Elasticity/ Polymer Network/ Supercoiling/ Deswelling/ Trapped Entanglement/ Mechanical Property/ Fractal Dimension

The elastic properties of the deswollen polymer networks, which are prepared by removing solvent from the network crosslinked in solution (deswelling), are still an unsettled subject in the physics of rubber elasticity [1]. The deswelling process is accompanied by the collapse of the network-chain conformation due to the volume decrease of material, which complicates the quantitative understanding of the elasticity of deswollen networks. The contraction of polymeric network chains on deswelling has often been called "supercoiling" [1]. The supercoiled chains are assumed to have the contracted conformation relative to the Gaussian chains, but the details on the conformation of supercoiled chains and the effects of supercoiling of network chains on the mechanical properties of deswollen networks are not well-known.

Another topic for the deswollen polymer networks is that the deswollen networks prepared from the solution with low polymer concentration can exhibit the remarkable high extensibility in comparison with the conventional elastomers [2,3]. The upper limit of extensibility for the crosslinked rubber can be roughly evaluated by the following equation.

$$\lambda_{max} \approx bN_e / (bN_e^{1/2}) = N_e^{1/2} \quad (1)$$

Here, λ_{max} is the elongation at break, and b is the Kuhn segment length, and N_e is the number of Kuhn segment between the neighboring crosslinking points when the trapped entanglement points are treated similarly as the chemical crosslinks. The trapped entanglements are the physical crosslinking points created by the uncrossability of mutual network chains. Since the typical value of N_e in the polymer melt is 20~40, λ_{max} is limited to 4~6. This value of λ_{max} explains well the fact that λ_{max} for

STATE AND STRUCTURES — Polymer Condensed States —

Scope of research

Attempts have been made to elucidate the molecular arrangement and the mechanism of structural formation / change in crystalline polymer solids, polymer gels and elastomers, polymer liquid crystalls and polymer composites, mainly by electron microscopy and X-ray diffraction / scattering. The major subjects are: synthesis and structural analysis of polymer composite materials, preparation and characterization of polymer gels and elastomeric materials, structural analysis of crystalline polymer solids by direct observation at molecular level resolution and in situ studies on structural formation / change in crystalline polymer solids.

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conventional elastomers rarely exceeds 10. The restriction of λ_{max} mainly originates from the existence of the large amount of the trapped entanglement which acts similarly as the chemical crosslinks. Equation (1) means that the enhancement of λ_{max} needs the increase of N_e, namely, the decrease of the amount of trapped entanglement. To crosslink the polymer chains at the solution state is a simple method to increase N_e. The value of Ne increases with decreasing ϕ_o as $N_e \sim \phi_o^{-1}$ where ϕ_o is the polymer volume fraction at the preparation state [4]. Furthermore, it should be noticed that the deswelling process causes the reduction of end-to-end distance (R) of network chains at undeformed state due to the large volume change. If the crosslinking points move affinely on deswelling, the value of R at undeformed state ($R_o=bN^{1/2}$) is reduced to $R_o \phi_o^{1/3}$. The value of λ_{max} for the deswollen networks prepared at ϕ_o is evaluated as follows.

$$\lambda_{max} \approx bN_e \phi_o^{-1} / (bN_e^{1/2} \phi_o^{-1/2} \phi_o^{1/3}) = N_e^{1/2} \phi_o^{-5/6} \quad (2)$$

Equation (2) means the value of λ_{max} for the deswollen networks prepared at 10% solution reaches 30~40 which is ca. 7 times as large as that of the networks crosslinked at melt state.

We have prepared the deswollen polymer networks by means of the endlinking reaction between vinyl-terminated polydimethylsiloxane (PDMS) and tetradimethylsiloxysilane in toluene. The value of ϕ_o was varied from 0.0877 to 1. The weight average molecular weight of PDMS is 47000.

Figure 1 shows the stress (σ_e) - elongation (λ) curve for the deswollen PDMS network prepared at ϕ_o=0.0877. Here, σ_e is the stress per the cross-sectional area at undeformed state. As can be seen, the deswollen PDMS network with ϕ_o=0.0877 shows a remarkable high extensibility reaching $\lambda_{max} \approx 18$. And we have confirmed that the deswollen network exhibits the almost complete elastic recovery. The theoretical value of λ_{max} for the deswollen PDMS network with ϕ_o=0.0877 is evaluated to be λ_{max}=20 per the above discussion together with the consideration for the stiffness of PDMS chain. The experimental result (λ_{max}=18) is found to be close to the theoretical limit.

We indicate the double logarithmic plots of σ_e vs.

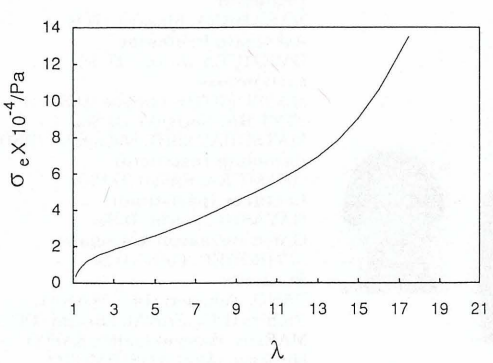

Figure 1. Stress-elongation curve of deswollen PDMS network prepared at ca. 9% solution.

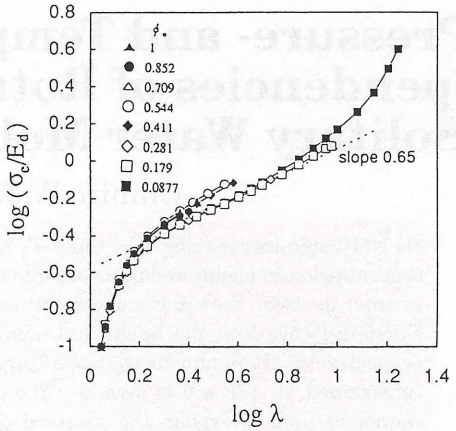

Figure 2. Double logarithmic plots of stress vs. elongation for deswollen PDMS networks.

λ for the deswollen networks in Figure 2. The stress is renormalized by E_d of each sample. Here, E_d is the initial Young's modulus. It is found that the stress-elongation relations of deswollen networks are divided into two groups: the networks prepared at $\phi_o \leqq 0.281$, and those at $\phi_o \geqq 0.411$. The overlapping of the curves suggests that the deswollen networks in each group have the common topological features. The major difference of the curves in each group is only in the extensibility. The dependence of σ_e on λ for the deswollen networks with $\phi_o \leqq 0.281$ is found to obey $\sigma_e \sim \lambda^{0.65}$ in the region $2.1 \leqq \lambda \leqq 5.5$. We regard this region $2.1 \leqq \lambda \leqq 5.5$ as the disentanglement process of the supercoiled structure, and estimate the fractal dimension (D) of the supercoiled structure from the dependence of σ_e on λ on the basis of the treatment of the large deformation for a flexible polymer chain by Pincus [5]. According to the concept of Pincus blob, the stress-elongation relation in the elongational process of the polymer chain with D is described by the following equation [1,5].

$$\sigma_e \sim \lambda^{D-1} \quad (3)$$

The value of D for the supercoiled structure is evaluated to be 2.5 from this equation [3]. This fractal dimension (D=2.5) is larger than D=2 for the Gaussian chain, while that is smaller than D=3 or 4 for the "polymer chain in an array of obstacles" (PCAO) model. The PCAO is one of the models describing the strongly collapsed conformation of polymer chains [6]. Our experimental result suggests that the supercoiled chain is contracted in comparison with the Gaussian one, while it is not collapsed as strongly as the PCAO models.

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